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IRON-NICKEL ALLOY WITH LOW COEFFICIENT OF THERMAL EXPANSION FOR MAKING SHADE MASKS

5   Field of the invention

The present invention relates to an iron and nickel based alloy with a very low coefficient of expansion that can be used in particular for manufacturing shade
10 or shadow masks for color display cathode ray tubes.

Prior art

In order to avoid the local deformation through thermal
15 expansion of the shadow masks used for color display cathode ray tubes, it is desirable for their manufacture to employ an alloy that has the lowest possible coefficient of thermal expansion. Thus, for example, use is made of an FeNi alloy containing about
20 36% nickel and about 0.3% manganese, well known by the name of Invar. Such an alloy has a coefficient of thermal expansion between 20°C and 100°C of the order of 1×10^{-6}/K.

25 However, this coefficient of expansion is still too high for certain applications, such as application to flat screens, and it has been proposed that use be made of an FeNi alloy in which a few % of the nickel are replaced with cobalt. This alloy has the advantage of
30 having a coefficient of thermal expansion of the order of 0.4×10^{-6}/K, which leads to a saving of 60%, but has the disadvantage of containing cobalt. The problem with this is that shadow masks are metal sheets pierced with very fine holes obtained by chemical etching, and the
35 cobalt leads to troublesome contamination of the chemical etching baths. Furthermore, cobalt is a very expensive element and it is desirable to reduce its content as far as possible.

Hence, it has been proposed that use be made of an FeNi alloy with a low residual and cobalt content, containing in particular under 0.1% manganese. This alloy has the advantage, on the one hand, of containing
5   little or no cobalt and, on the other hand, of having a coefficient of thermal expansion of the order of $0.8 \times 10^{-6}/K$, which is lower than that of the conventional FeNi alloy (Invar). However, the coefficient of expansion is still too high, particularly for large format or
10   slimline flat screens.

Furthermore, it is desirable to use thinner masks so as to reduce their cost of manufacture and so as to improve the quality and precision of the images. Now,
15   the mechanical properties of the alloys of the prior art are not good enough to allow the thickness of the masks to be reduced while at the same time keeping the masks to withstand the deformations that may arise during the various transport and handling steps.
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Summary of the invention

The object of the present invention is to remedy the disadvantages of the alloys of the prior art by
25   proposing an alloy that can be used in particular for the manufacture of shadow masks, that contains little or no cobalt, of which the coefficient of thermal expansion is lower than that of the known FeNi alloys, and which has an elastic limit in the annealed state
30   that is maintained or even improved.

To this end, a first subject of the invention is an alloy, the chemical composition of which comprises, by weight:
35                          $35\% \leq Ni \leq 37\%$
                            $0.001\% \leq C \leq 0.05\%$
                            $Mn \leq 0.10\%$
                            $Si \leq 0.15\%$
                            $Co \leq 0.5\%$

$$S<0.002\%$$
$$P<0.006\%$$
$$B\leq0.0005\%$$
$$Al+Mo+Cu+Cr\leq0.15\%$$
5          $$0.015\%\leq2(V+Ti)+Nb+Zr+Ta+Hf\leq0.2\%$$
$$0.0025\%\leq N+O\leq0.015\%$$

possibly calcium and/or magnesium in a total content of between 0.0001 and 0.005%,

10   the remainder consisting of iron and inevitable impurities resulting from the production process.

Description of the preferred embodiments

15   In a preferred embodiment, the alloy furthermore exhibits a niobium content of below 0.1%, or even below 0.07%.

In another preferred embodiment, the alloy exhibits a
20   carbon content of above 0.0035%.

In another preferred embodiment, the alloy exhibits a grain size below 10, or even below 9 (in accordance with G ASTM E 112).
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In another preferred embodiment, the alloy has a coefficient of thermal expansion between 20°C and 100°C of below 0.70×10^{-6}/K, and preferably of below 0.65×10^{-6}/K. In any case, the coefficient of expansion
30   obtained is below 0.75×10^{-6}/K.

In another preferred embodiment, the alloy exhibits a conventional elastic limit at 0.2% OYS, in the annealed state, of above 250 MPa, preferably above 280 MPa, and
35   as a more particular preference, above 300 MPa, or even 310 MPa.

In another preferred embodiment, the niobium and carbon contents of the alloy composition are such that:

$$Nb \times C \leq 0.01.$$

This embodiment allows the elastic limit of the grade in the annealed state to be improved through the formation of carbides on a sub-micron scale.

In another preferred embodiment, the titanium, niobium and nitrogen contents of the alloy composition are such that:

$$Ti \times N \leq 0.00006$$
$$Nb \times N \leq 0.001.$$

This embodiment makes it possible to avoid the presence of excessive quantities of niobium and/or titanium nitrides, which have a size of the order of a few hundred nanometers or even a few microns, and which present problems when manufacturing the shadow masks by etching.

In another embodiment, the alloy contains precipitates based on titanium and/or on niobium and/or on vanadium and/or on tantalum and/or on zirconium and/or on hafnium, the mean size of which is equal to 100 nm or smaller, preferably equal to 70 nm or smaller and as a more particular preference, smaller than 50 nm.

A second subject of the invention is a method of manufacturing a strip of alloy, according to the invention comprising the steps whereby:

- a semi-finished version of said alloy is hot-rolled after reheating to a temperature of above 850°C and below 1350°C so that the rolling temperature is above the solutionizing temperature of the titanium- and/or niobium- and/or vanadium- and/or zirconium- and/or tantalum- and/or hafnium-based precipitates and so that the temperature at the end of rolling is below the temperature at which said precipitates begin to precipitate, so as to obtain a hot-rolled strip;

- the hot-rolled strip is cold-rolled in one or more passes to obtain a cold-rolled strip, possibly with one or more intermediate annealing operations between two passes.

In a first preferred embodiment, the temperature of the intermediate annealing operation or operations performed during the cold-rolling is below the solutionizing temperature of said precipitates.

In a second preferred embodiment, the temperature of the intermediate annealing operation or operations performed during the cold-rolling is above the solutionizing temperature of said precipitates.

These two different embodiments allow the formation of precipitates and the grain size to be altered. By way of nonlimiting indication, a grain size larger than 7 is generally obtained for the first embodiment, whereas grain sizes smaller than 7.5 are generally obtained in the second embodiment.

In another preferred embodiment, the temperature at the end of hot-rolling is equal to 850°C or lower, which makes it possible to obtain finer grains.

A third subject of the invention is the use of the alloy described hereinabove for the manufacture of shadow masks for color display cathode ray tubes, for the manufacture of shadow masks held in the vertical or horizontal direction for flat screen monitors, for the manufacture of shadow mask support frames, for the manufacture of cryogenic storage containers, and also for the manufacture of electron gun grids, by virtue of its very strong suitability for mechanical cutting.

The invention is based on the fact that the inventors discovered, in a novel way and surprisingly, that the precipitation of compounds formed from titanium and/or

niobium and/or vanadium and/or zirconium and/or
tantalum and/or hafnium, on the one hand, and from
carbon, oxygen and/or nitrogen, on the other, leads to
an appreciable reduction in the coefficient of
expansion when the alloy has a low Si and Mn content.
Precise analysis of the compounds formed is tricky, but
in particular carbides, nitrides, carbonitrides, oxides
and/or oxynitrides of the abovementioned metals are
found.

Without wishing to be tied to a theory, the inventors
believe that this effect could be due to the fact that
these various compounds, for the most part, have a
crystalline structure of the cubic type, and form
precipitates the size of which is generally of the
order of several tens of nanometers when they are
formed in the solid phase. These small-sized
precipitates precipitate in the matrix and not at the
grain boundaries, as is conventionally the case.

This effect on the coefficient of expansion of the
alloy is particularly visible in Figure 1, which
represents the variations of this coefficient between
20 and 100°C as a function of the sum of the oxygen and
nitrogen contents, for an alloy the composition of
which contains titanium at contents ranging between
0.01 and 0.05%, less than 5 ppm of boron, less than
5 ppm of sulfur and no aluminum. The same effect is
obtained with an alloy containing niobium completely or
partially replacing the titanium, within the limits set
by claim 1.

The alloy according to the invention contains, as % by
weight:
-       from 35% to 37% nickel, and preferably between
        35.5% and 36.5%, so as to obtain a low coefficient
        of thermal expansion between 20°C and 100°C,
-       from 0.001% to 0.05% of carbon, so as to form fine
        carbide precipitates. The formation of

nanometer-scale carbide precipitates has the effect of reducing the coefficient of expansion and of improving the mechanical properties of the product. Its content is limited to 0.05% so as to avoid the formation of large insoluble carbide inclusions. It is preferable for the carbon content to be above 0.0035% so as to have enough of a carbon content by volume to obtain improved mechanical characteristics. It is also preferable for the carbon content to be kept to a value below 0.010%, or even below 0.007% so as to further limit the size of the carbides formed.

- under 0.1% manganese because this element increases the coefficient of expansion of the alloy and needs to be limited,

- under 0.15% silicon, because this element increases the coefficient of expansion of the alloy and needs to be limited,

- under 0.5% cobalt, so as not to contaminate the chemical etching baths used to etch the shadow masks,

- possibly 0.0001 to 0.005% of at least one element taken from among calcium and magnesium so as to trap the sulfur which always exists by way of an impurity and thus ensure good hot-deformation ability,

- possibly sulfur at a content of below 0.002% so as not to impair the hot-conversion ability of the alloy,

- possibly phosphorus in a content of below 0.006% so as not to impair the hot-conversion ability of the alloy,

- possibly boron at a content of less than 0.0005%, and preferably of 0%: this is because the inventors have found that with boron present, the coefficients of thermal expansion increase appreciably,

- possibly aluminum, molybdenum, copper or chromium in a total content of less than 0.15%, because

these elements increase the coefficient of thermal expansion of the alloy,

- titanium, vanadium, niobium, tantalum, zirconium and/or hafnium in quantities such that the sum 2(V+Ti)+Nb+Ta+Zr+Hf lies between 0.015% and 0.2% so as to be able to form precipitates based on these elements, these precipitates preferably exhibiting a mean size smaller than 100 nm, and as a preference smaller than 70 nm, and as a particular preference, smaller than 50 nm. It is furthermore preferable for the niobium content to be below 0.1%, or even below 0.07%, so as to further reduce the coefficient of expansion and the size of the precipitates,

- oxygen and/or nitrogen in quantities such that the sum of their contents lies between 0.0025% and 0.015%, because the inventors have found, in a novel way, that the presence of oxygen and/or of nitrogen in these contents in the alloy allows the coefficient of expansion to be lowered when it is associated with the presence of titanium and/or niobium and/or vanadium and/or tantalum and/or zirconium and/or hafnium. The sum of these contents is limited to 0.015% so as to avoid the formation of large oxides or nitrides,

- the remainder of the composition is made up of iron and of impurities resulting from the production process.

The alloy may be formulated, for example, in an arc furnace with an AOD or VOD converter refining phase; it may also be formulated in an induction furnace under vacuum. This formulation must be carried out in such a way as to obtain the desired residual contents.

The alloy is then cast into the form of a semi-finished product such as an ingot, a billet or a remelting electrode. It may also be cast directly in the form of a thin slab or thin strip less than 15 mm thick, and

preferably with a thickness of between 8 and 12 mm.

When the alloy is cast in the form of a remelting electrode, this electrode is remelted under
5   electrically-conducting slag so as to obtain better homogeneity of the chemical composition and of the solidification structure.

The semi-finished product or the thin strip obtained by
10   direct casting is then hot-rolled at a temperature of above 850°C, and preferable above 1150°C but below 1350°C to obtain a hot-rolled strip with a thickness of generally between 2 mm and 6 mm, and preferably between 3 and 5 mm, which is then cold-rolled in one or more
15   passes, possibly with annealing operations above 800°C. The temperature to which the strip is heated between the hot-rolling or cold-rolling steps may be chosen in such a way that the precipitates of oxides, carbides, or nitrides may possibly be returned to solution. Rapid
20   coolings may also be applied in order to keep these elements likely to form precipitates in solid solution within the alloy. Equilibrium precipitation treatments may then be carried out by temperature soaks at between 750°C and 1200°C (but preferably below 1050°C).
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The invention will now be described in greater detail but without implying limitation, and illustrated by examples.

30   Tests

By way of example, the alloys identified 1 to 16 according to the invention and 17 to 23 by way of comparison and the composition of which is described in
35   Table 1 below were produced. The chemical compositions and the coefficients of expansion α between 20 and 100°C were measured on test specimens taken from the hot-rolled strips. Each of these test specimens was annealed for 30 minutes at 950°C, and cooled in ambient

air before the coefficient of thermal expansion measurements were taken. The results of the tests are collated in Table 2, in which the coefficient of expansion α is expressed in 10^{-6}/K.

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The etching tests were performed on cold-rolled products from the experimental castings, partially coated with photosensitive resin. The etchings were performed at 60°C with an $FeCl_3$ solution having a

10   density of 45.5°Bé. The quality of the etching was evaluated by measuring the regularity of the cut contours, and through the presence of defects associated with the presence of particles.

Table 1

	No.	Ni	Mn	Si	Al	Co	C	S	N	O	Nb	V	Ti	B
Examples according to the invention	1	35,80	0,048	<0,007	0,009	0,011	0,003	0,0010	0,0036	0,0019	<0,005	<0,005	0,023	<0,0005
	2	35,84	0,044	<0,007	<0,005	0,010	0,003	0,0010	0,0016	0,0024	<0,005	<0,005	0,017	<0,0005
	3	36,08	0,027	0,021	<0,005	0,010	0,002	<0,0005	0,0023	0,0041	<0,005	<0,005	0,012	<0,0005
	4	36,13	0,027	0,011	<0,005	0,009	0,003	<0,0005	0,0020	0,0016	<0,005	<0,005	0,034	<0,0005
	5	36,08	0,029	0,053	<0,005	0,011	0,003	0,0005	0,0030	0,0024	<0,005	<0,005	0,024	<0,0005
	6	36,16	0,030	0,078	<0,005	0,010	0,003	0,0005	0,0031	0,0012	<0,005	<0,005	0,048	<0,0005
	7	36,09	0,031	0,020	0,044	0,009	0,003	<0,0005	0,0026	0,0013	<0,005	<0,005	0,022	<0,0005
	8	36,06	0,030	0,021	0,055	0,010	0,002	<0,0005	0,0028	0,0010	<0,005	<0,005	0,052	<0,0005
	9	36,10	0,040	0,045	0,008	0,050	0,004	0,0009	0,0023	0,0018	0,030	<0,005	0,016	<0,0005
	10	36,10	0,045	0,040	<0,005	0,048	0,004	0,0008	0,0030	0,0015	<0,005	0,020	0,010	<0,0005
	11	36,15	0,040	0,030	<0,005	0,050	0,004	0,0008	0,0032	0,0017	0,040	<0,005	<0,005	<0,0005
	12	36,20	0,042	0,033	<0,005	0,035	0,003	0,0009	0,0030	0,0015	0,028	<0,005	0,015	<0,0005
	13	36,15	0,041	0,032	<0,005	0,050	0,003	0,0010	0,0026	0,0017	0,035	<0,005	0,009	<0,0005
	14	36,18	0,051	0,027	0,008	0,014	0,004	0,0009	0,0021	0,0012	0,060	<0,005	0,015	<0,0005
	15	36,0	0,06	0,03	<0,005	0,28	0,0044	0,0007	0,0031	0,0012	0,051	<0,005	<0,005	<0,0005
	16	36,1	0,03	0,025	0,006	0,05	0,0048	0,0005	0,0025	0,0015	0,055	<0,005	<0,005	<0,0005
Comparative Examples	17	35,84	0,052	<0,007	0,013	<0,005	0,003	0,0008	0,0042	<0,001	<0,005	<0,005	0,013	0,0010
	18	35,83	0,053	0,011	0,019	0,011	0,006	0,0006	0,0034	0,0012	<0,005	<0,005	0,025	0,0024
	19	35,79	0,049	<0,007	0,038	0,012	0,002	0,0028	0,0021	<0,001	<0,005	<0,005	0,045	<0,0005
	20	36,00	0,071	0,076	<0,005	0,049	0,005	0,0007	0,0025	0,0012	<0,005	<0,005	<0,005	<0,0005
	21	35,95	0,042	0,021	<0,005	0,068	0,002	0,0029	0,0013	0,0012	0,051	<0,005	<0,005	<0,0005
	22	35,80	0,039	<0,007	0,006	<0,005	0,002	0,0005	0,0010	0,0013	0,009	0,012	0,080	<0,0005
	23	36,2	0,045	0,041	<0,005	0,050	0,002	0,0008	0,0003	<0,001	0,040	<0,005	0,007	<0,0005

Table 2:

No.	Conventional elastic limit at 0.2% OYS (MPa)[1]	Mean coefficient of thermal expansion between 20 and 100°C	Quality of the etching [2]	Grain size[3] (annealed state)
1	300	0.53	P	8
2	297	0.57	G	8
3	307	0.52	G	8.5
4	300	0.52	P	8
5	298	0.56	P	8
6	292	0.61	P	7.5
7	301	0.62	P	8.5
8	291	0.59	P	7.5
9	332	0.57	G	9.5
10	327	0.54	G	9
11	320	0.49	G	8.5
12	328	0.56	G	9.5
13	322	0.50	G	9
14	325	0.61	G	9
15	285	0.54	G	6.5
16	289	0.51	G	6.5
17	289	0.80	G	8.5
18	298	1.01	P	8.5
19	295	0.76	P	8.5
20	275	0.75	G	8
21	302	0.75	G	8.5
22	290	0.77	P	8.5
23	313	0.78	G	9

[1]Values measured after a heat treatment for 15 minutes at 850°C.
[2]G: etching deemed to be good – P: presence of faults associated with the presence of particles.
[3] Grain size measured in accordance with G ASTM E 112, to plus or minus 0.5 of a unit.

In the light of this table, all the strips according to the invention can be seen to have a coefficient of expansion of below 0.70×10^{-6}/K and even of below 0.65×10^{-6}/K in most cases.

By contrast, the strips given by way of comparison have coefficients of expansion appreciably higher than 0.70×10^{-6}/K.

The comparative examples 17 and 18 show the detrimental effect of boron on the coefficient of expansion. The comparative examples 19 and 21 show the detrimental influence of sulfur on the coefficient of expansion. These comparative examples also show the importance that the oxygen and nitrogen contents have on the coefficient of expansion.

The comparative example 20 which corresponds to the conventional low-manganese FeNi alloy provides the reference that demonstrates the advantages of the invention. Specifically, in the absence of compounds allowing solid phase precipitates to form, the coefficients of expansion measured are higher.

Comparative example 21 shows the detrimental effect of sulfur on the coefficient of expansion.

Comparative examples 22 and 23 show the importance of the nitrogen and oxygen contents on the coefficient of expansion.

The alloy according to the invention can also be used for the manufacture of shadow mask support frames. This alloy has good behavior during chemical etching and this is associated with the controlled weak presence of residuals of the C,S,N type in solid solution, and because of its small amounts of micron-scale inclusions.